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TRANSITIONS IN POLY(VINYL FLUORIDE) AND POLY(VINYLIDENE FLUORIDE).

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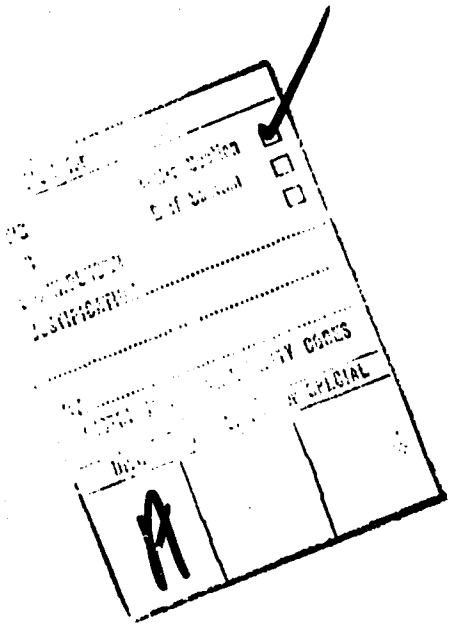
ABSTRACT

The temperature dependence of the argon permeability and diffusion coefficients in poly(vinyl fluoride) and poly(vinylidene fluoride) was determined experimentally. Two transitions were revealed as slope discontinuities in the Arrhenius plots of the transport parameters for argon in poly(vinyl fluoride). Only one transition however was observed in poly(vinylidene fluoride). A second transition reported in the literature using other techniques was below -30°C, the lowest temperature conveniently obtained in the existing experimental apparatus. The results are consistent with dilatometry data also reported in this paper and with literature values.



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Introduction

Among the many ways of determining the glass transition temperatures of polymers is the measurement of the permeabilities and diffusivities of gases as a function of temperature. A change of slope in the corresponding Arrhenius plots is observed at the glass temperature with most polymers. This was first clearly shown by the work of Meares[1,2] with poly(vinylacetate) and confirmed in subsequent work by others[3,4]. The activation energies are usually less in the glassy state than in the rubbery state and the reasons for this have been discussed[1-5]. However, the Arrhenius plots describing the temperature dependence of the diffusion coefficient for some particular polymers do not exhibit a discontinuity of slope at the Tg[5]. Transitions in semi-crystalline polymers are more complex and multiple transitions are more frequently observed than with amorphous polymers. Boyer has discussed this problem at length[6,7]. In particular, he has distinguished between two glass transitions (1) A relatively higher temperature transition, Tg(u), due to relaxations in the amorphous regions under restraint by the crystallites and (2) a lower temperature transition Tg(L) due to relaxations in amorphous regions essentially free from restraints. A number of transitions have been observed in poly(vinylfluoride) and poly(vinylidenefluoride) and it was considered worthwhile, therefore, to study the temperature dependence of gas transport in these two polymers. Poly(vinylfluoride) has been studied with hydrogen and deuterium by Ziegel et al.[8] A glass transition was found

at 45°C but the activation energies for diffusion were larger in the glassy state than in the rubbery state; this result is apparently the first example of such behavior. In this paper, the results of a study of the temperature dependence of the permeabilities and diffusivities of argon in both polymers in the temperature range of -32°C to +72°C are presented and discussed. Simple dilatometry measurements were also conducted in the same temperature range. Enns and Simha[9] have recently completed a more thorough and sophisticated dilatometric study of both polymers in the temperature range -30° to +200°C. They have also discussed and tabulated all the other reported transitions in the two polymers.

Experimental

Polyvinyl Fluoride A uniform film sample, 3.18×10^{-3} centimeters thick, was kindly supplied by Dr. R. F. Boyer, Dow Chemical Co. Midland, Michigan.

Polyvinylidene Fluoride. A sample of polyvinylidene fluoride, (Kynar 881) having a unimodal molecular weight distribution, and an Mn of 82,000, was kindly supplied by the Pennwalt Corporation, King of Prussia, Pennsylvania. It was dissolved as a 20% solution in dimethylformamide and cast at 150°C. The films were dried at 60°C under high vacuum to constant weight. The final film thickness was 5.21×10^{-3} centimeters.

Argon was obtained from the Matheson Co. and was 99.99% pure.

Dilatometry. A simple glass dilatometer was used with clean mercury as the displacing fluid. The chopped film sample was pumped out for several days at 10^{-5} torr and the mercury added for a small side arm. The whole assembly was then sealed and the measurements at each temperature read with a cathetometer. Details of the apparatus and the necessary corrections and calculations are

described elsewhere.[10] Measurements were taken over a temperature range of $-30^{o}C$ to $+98^{o}C$.

Gas Transport Measurements

The time lag method was used, full details of the method and the equipment may be found elsewhere.[10,11]

Results

The dilatometry data for both polymers are presented in Figure 1. Transition points of $37^{o}C$ and $25^{o}C$ are clearly shown for poly(vinylfluoride) and poly(vinylidenefluoride), respectively.

The argon permeabilities and diffusivities for polyvinyl fluoride are shown in Figures 2 and 3, respectively. The permeability data show a weak transition at $44^{o}C$ and a more pronounced transition at $-19^{o}C$. The diffusivity data suggest somewhat more definite transitions at rather similar temperatures. The changes in slope are consistent with most of the reported data regarding the effect of Tg on the observed temperature dependence of the transport parameter. Specifically lower activation energies for diffusion are associated with glassy state diffusion of argon in poly(vinylfluoride).

The temperature dependence of the permeabilities and diffusivities for argon in poly(vinylidenefluoride) are shown in Figures 4 and 5, respectively. In spite of considerable scatter, a weak change in slope is apparent in the Arrhenius plot of the permeability data at about $24^{o}C$. A much more distinct change in slope at the same temperature is apparent in the corresponding plots of the diffusivity data,again the activation energies were lower below the transition temperature.

Discussion

Polyvinyl Fluoride

The dilatometry data clearly indicated a transition at $38^{o}C$ compared with a value of $50^{o}C$ found by Enns and Simha, using a more sophisticated

dilatometry technique. Ziegel, et at[8] in a study of hydrogen isotope transport found no transition with the permeabilities but a transition of 45°C with the diffusion data. However, the activation energy below the transition point was considerably greater than above. In this regard, permeability data is often less sensitive than diffusion data, especially with small size penetrants such as hydrogen or helium. The slopes of Arrhenius plots for diffusion coefficients also change very little at the known transition points with helium or hydrogen but the Zeigel et al[8] results are the first reported demonstration of an activation energy being greater in the glassy state than in the rubbing state.

The Arrhenius plots characterizing argon transport, a considerably larger penetrant are presented as Figures 2 and 3 and show breaks in the slopes at 45.5°C and -19°C. The change of slopes indicate a higher activation energies at temperatures above both breaks. The reasons for the unusual results found by Ziegel et al, are not clear. Transitions in the vicinity of 40-5-°C have been observed by many authors and have been ascribed to the Tg(u) trarsition suggested by Boyer[7] and by Enns and Simha[9]. The other transition observed between -15 and -20°C has been ascribed by the same authors to be the Tg(L) temperature. The argon transport data are the first to be reported with a larger penetrant than hydrogen and it is gratifying that transitions at the normal temperatures were observed with the activation energy for diffusion higher in the rubbery state than in the glass. The reasons for the lower transition temperature found with dilatometry are not known. It could not be due to differences in the sample since both the dilatometry and transport measurements were conducted on film taken from the

same piece. Both transitions are well within the range of reported values.[7,9]

Polyvinylidene Fluoride

There is a close agreement between the transition temperatures of 25°C obtained by dilatometry and 24°C suggested by the argon transport data. Enns and Simha[9] observed a transition at 23°C for both an annealed sample and a sample quenched from the melt to 25°C. The transition was not observed, however, with a sample quenched to 0°C. Boyer had concluded from the available that Tg(u) was in the vicinity of 20°C[7]. The present work is the first determination reported using gas transport data to characterize thermal transitions in poly(vinylidenefluoride) and is in good agreement with the literature. Presumably, the Tg(L) transition is below -30°C which is beyond the range of both dilatometry and transport measurements.

Argon Transport Parameters

The pre-exponential factors and activation energies characterizing permeation and diffusion in poly(vinylfluoride) and poly(vinylidene fluoride) are listed in Table I with the values of the permeabilities and diffusivities determined at 25°C. The activation energies are in the normal range found for many polymers. Both polymers are excellent gas barriers at ambient temperatures with permeabilities in the same range as unplasticized poly(vinylchloride).[12]

Acknowledgements

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Table I.

ARGON TRANSPORT PARAMETERS FOR POLY(VINYL FLUORIDE) AND POLY(VINYLIDENE FLUORIDE)

Parameter	Polyvinyl Fluoride			Polyvinylidene Fluoride	
	Above Tg(u)	Tg(u) - Tg(L)	Below Tg(L)	Above Tg(u)	Tg(u)-Tg(L)
Temperature Range	98°C-44°C	44°C- -19°C	-19°C- -30°C	98°C-24°C	24°C - - 30°C
$P_{25°C}$	2.0×10^{-12}	-	-	3.5×10^{-2}	-
$P_{25°C}$	3.2×10^{-9}	-	-	4.0×10^{-9}	-
P_o	2.2×10^{7}	1.8×10^{2}	4.2×10^{-2}	3.7×10^{-2}	3.6×10^{-3}
E_p	22.0	14.6	10.5	13.7	12.3
D_o	2.8	4.5×10^{-2}	3.7×10^{-6}	4.3×10^{2}	2.0
E_d	16.6	14.2	9.4	15.0	11.8

CAPTIONS FOR FIGURES

Figure 1. Specific volume versus temperature plots for poly(vinyl fluoride) and poly(vinylidene fluoride)

Figure 2. Arrhenius Plot of the permeability constants for Argon in poly(vinyl fluoride)

Figure 3. Arrhenius Plot of the Diffusion Constants for Argon in Poly(vinyl fluoride)

Figure 4. Arrhenius Plot of the Permeability Constants for Argon in Poly (vinylidene fluoride)

Figure 5. Arrhenius Plot of the Diffusion Constants for Argon in Poly(vinylidene fluoride)

Fig. 1

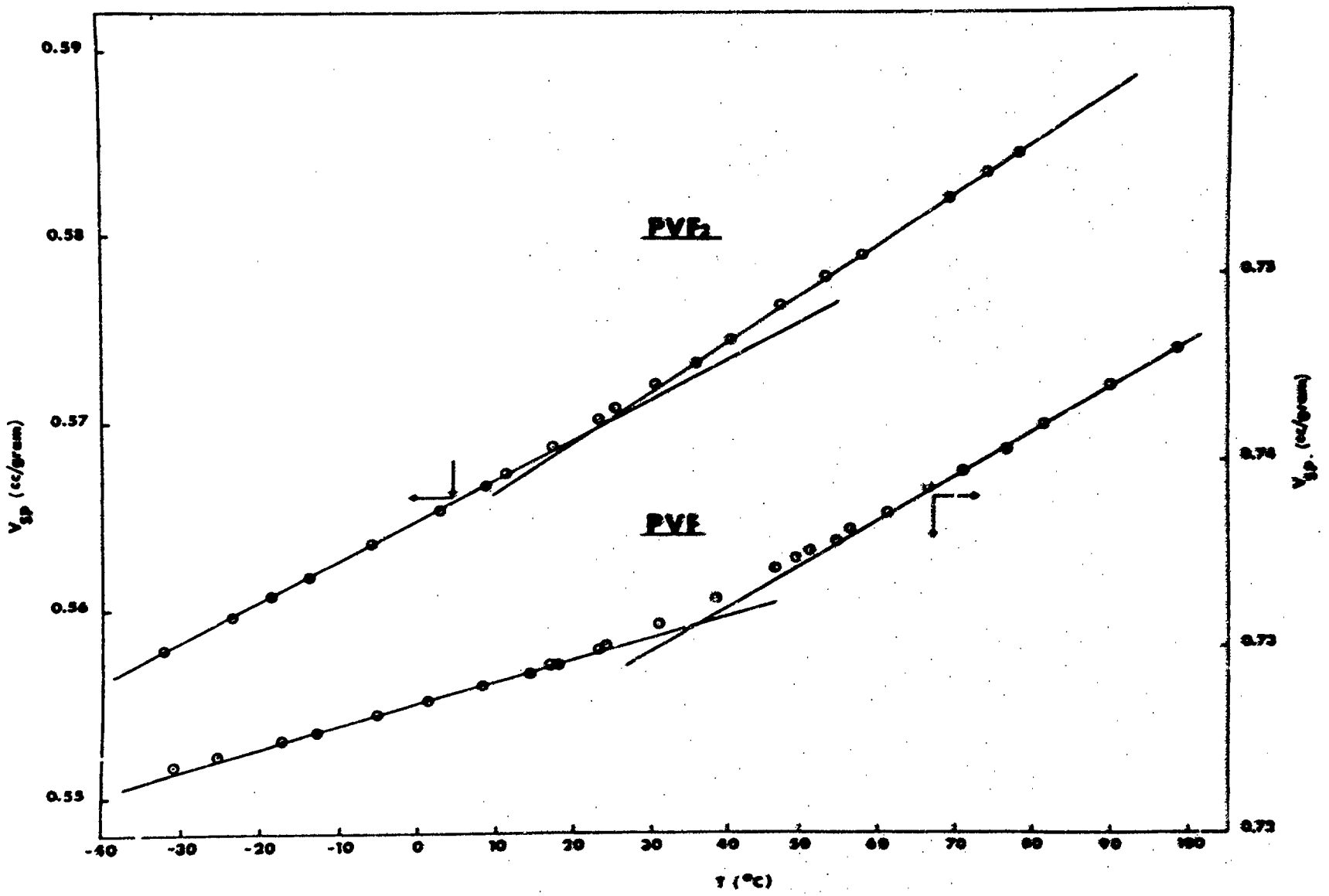
0.59
0.58
0.57
0.56
0.55
V_{sp} (cc/gram)
PVF₂
PVF
0.75
0.74
0.73
0.72
V_{sp} (cc/gram)
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
90
100
T (°C)

Fig. 2

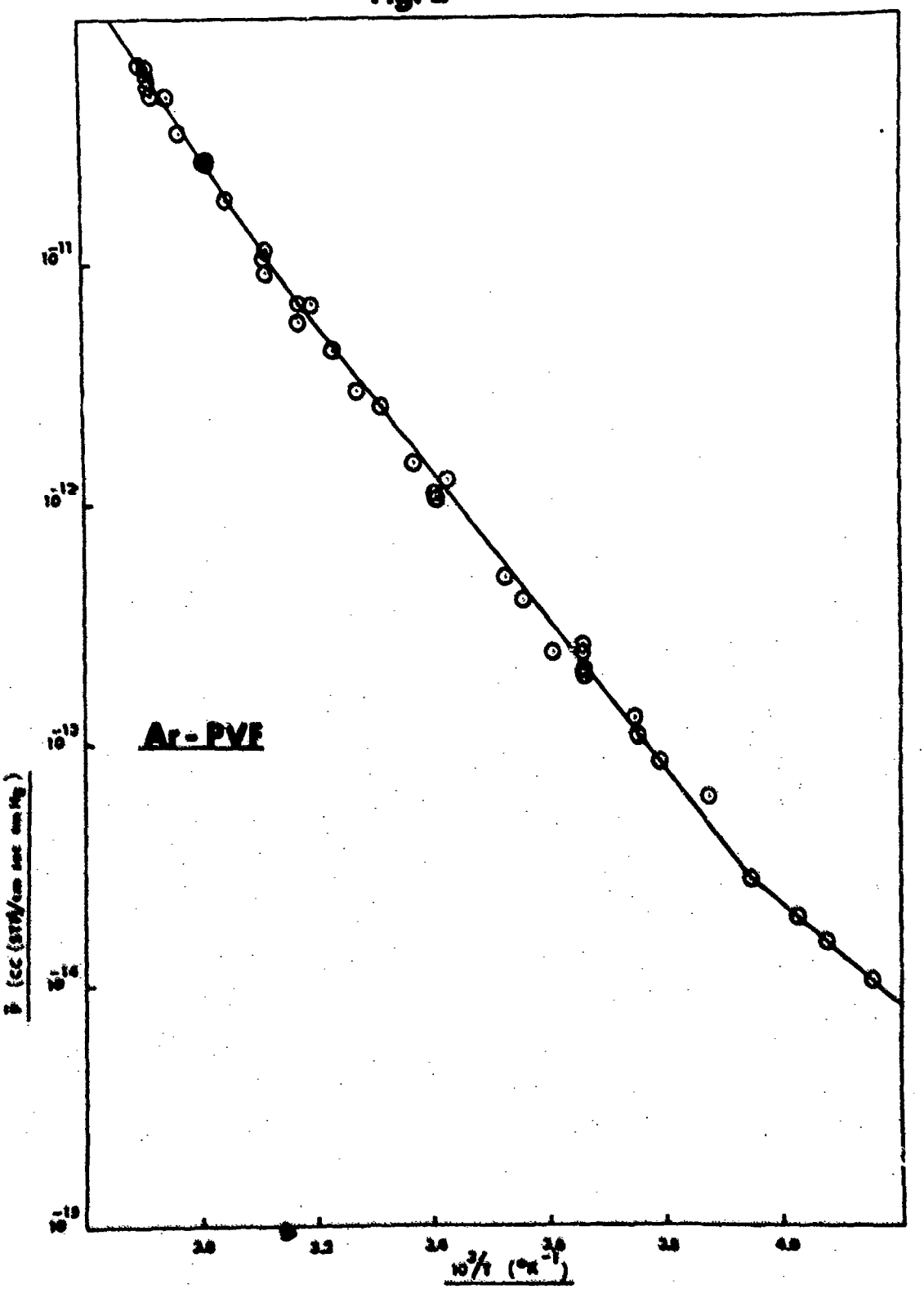

Fig. 3

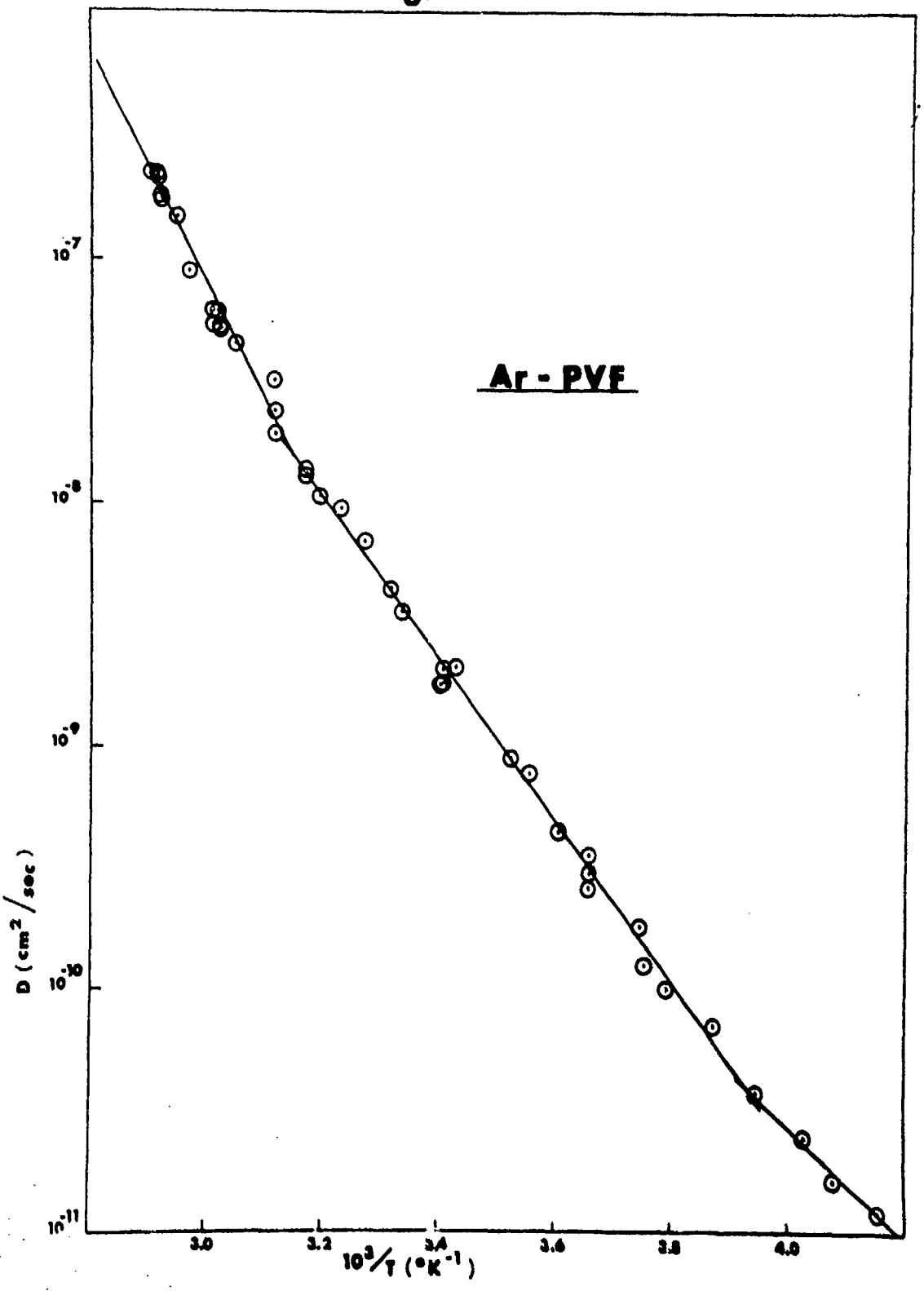

Fig. 4

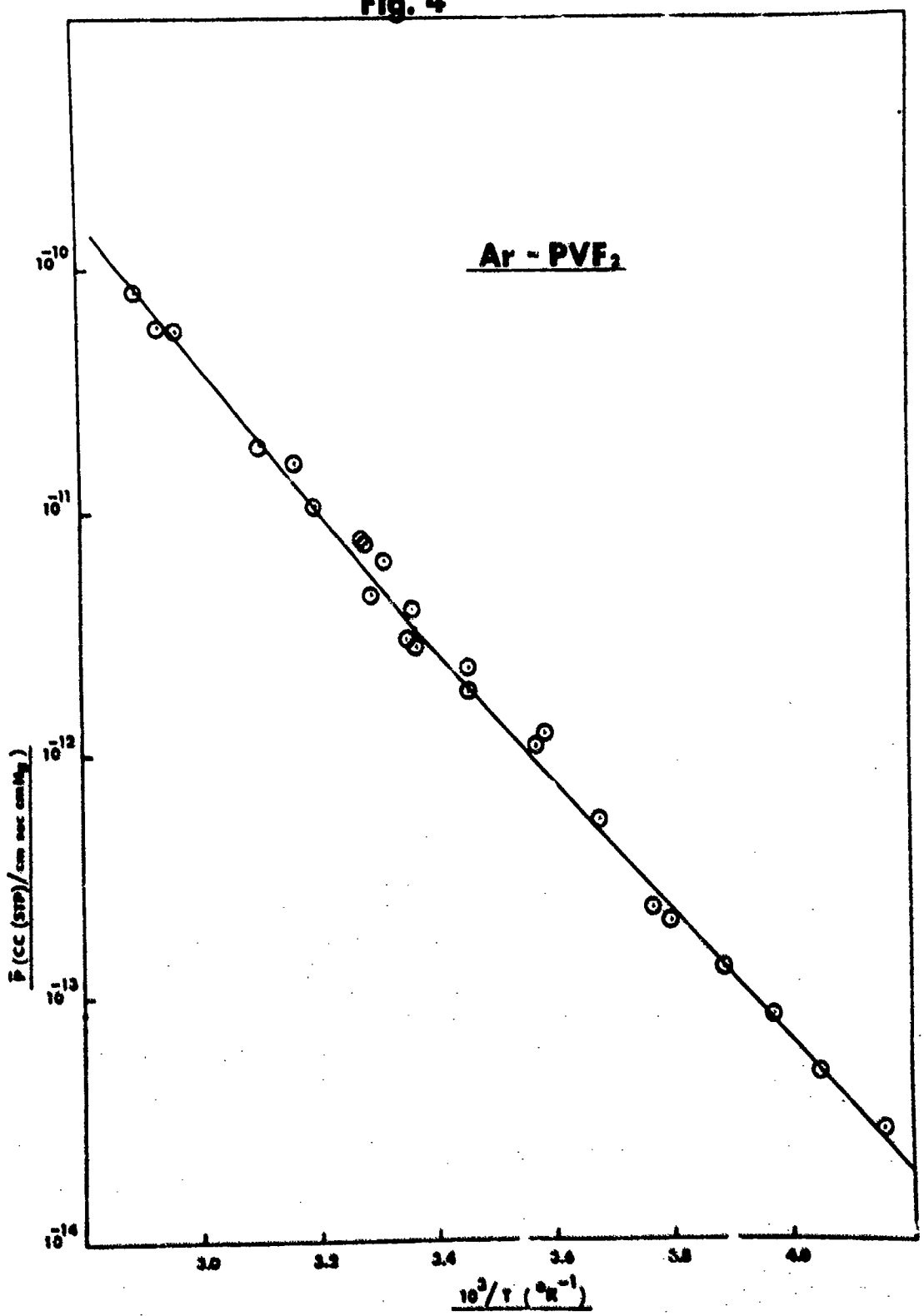
Ar - PVF2
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
$\bar{P}$ (cc (STP)/cm sec cmHg)
3.0
3.2
3.4
3.6
3.8
4.0
$10^3/T$ ($^oK^{-1}$)

Fig 5